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# ESTABLISHMENT OF NATIONAL EMISSION STANDARDS FOR STATIONARY SOURCES. VOLUME IV. SULFURIC ACID PLANTS

H. L. Hamilton, Jr., et al

Research Triangle Institute
Durham, North Carolina

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# ESTABLISHMENT OF NATIONAL EMISSION STANDARDS FOR STATIONARY SOURCES

## Volume IV Sulfuric Acid Plants

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## 1.0 INTRODUCTION

Sulfuric acid is one of the largest volume industrial chemicals produced in the United States. Production capacity totals approximately 38 million short tons and is accounted for by 250 plants of which about 215, representing over 97% of the production capacity, are of the contact process type; the remainder are the older lead chamber process plants. Actual U.S. sulfuric acid production in 1968 was 28.5 million short tons.[1] Production is estimated to increase to 54 million and 88 million short tons by the years 1980 and 1990 respectively.[2]

Sulfuric acid is produced in a variety of concentrations and in four grades: commercial; electrolyte or high purity; textile (having low organic content); and C.P. or reagent grade. Its chief uses are in the production of fertilizer, manufacture of chemicals, oil refining, pigment production, iron and steel processing, synthetic fiber production, and in metallurgical applications.

Most acid is consumed near its point of manufacture, either by the producer or by nearby industries. Very little sulfuric acid is shipped more than 200 to 300 miles. Approximately 40% of the sulfuric acid plants producing about 1/3 of the annual United States production are located within established Air Quality Control Regions.

The sulfur bearing raw materials for contact sulfuric acid plants come from a variety of sources. Most of the sulfuric acid in the United States is produced from elemental sulfur. The remaining acid is made from iron pyrites; tail gas from lead, copper, and zinc smelters; hydrogen sulfide; and spent alkylation acid from petroleum refineries. The few remaining chamber process plants use only elemental sulfur.

Contact sulfuric acid plants emit sulfur dioxide, sulfuric acid mist and small amounts of sulfur trioxide. Depending upon the sulfur bearing feed stock and plant operating conditions, they may also emit nitrogen oxides. In the chamber process, nitrogen oxides in addition to sulfur oxides and acid mist, are regularly emitted.

Concentrations of sulfur dioxide emitted from contact sulfuric acid plants, excluding dual absorption, vary between 1500 and 6000 ppm by volume; acid mist emissions vary between 2 and 20 mg/SCF for sulfur burning plants and between 5 and 50 mg/SCF for "wet gas" plants; and $SO_3$ emissions are normally between 0.3 and 1.3 ppm. For chamber process plants, sulfur dioxide emission concentrations vary between 1500 and 4000 ppm; acid mist varies between 5 and 50 mg/SCF; and NO and $NO_2$ emissions are approximately 500 ppm and 1000 ppm respectively.

## 2.0 PROCESS DESCRIPTION

Sulfuric acid plants can be broadly classified as either chamber plants, contact plants burning elemental sulfur, or "wet gas" contact plants. This latter "wet gas" classification refers in this report not only to those plants where the gas from the furnace is not dried, but to all contact sulfuric acid plants which do not use elemental sulfur as the feed stock.

### 2.1 Chamber Process

Chamber process plants are gradually disappearing because of the low concentration of the product acid (about 78%), the high cost of operation, and the emissions of nitrogen oxides. No new chamber process plants have been built since 1956 and the fewer than 40 remaining units in the United States account for only a few percent of the total sulfuric acid production.

Figure 1 is a schematic of a typical lead chamber plant using elemental sulfur as a raw material. In this plant the hot sulfur dioxide gas flows through the Glover tower, then through several lead chambers in series, and finally through one or more Gay Lussac towers from which the waste gas passes through a stack to the atmosphere.

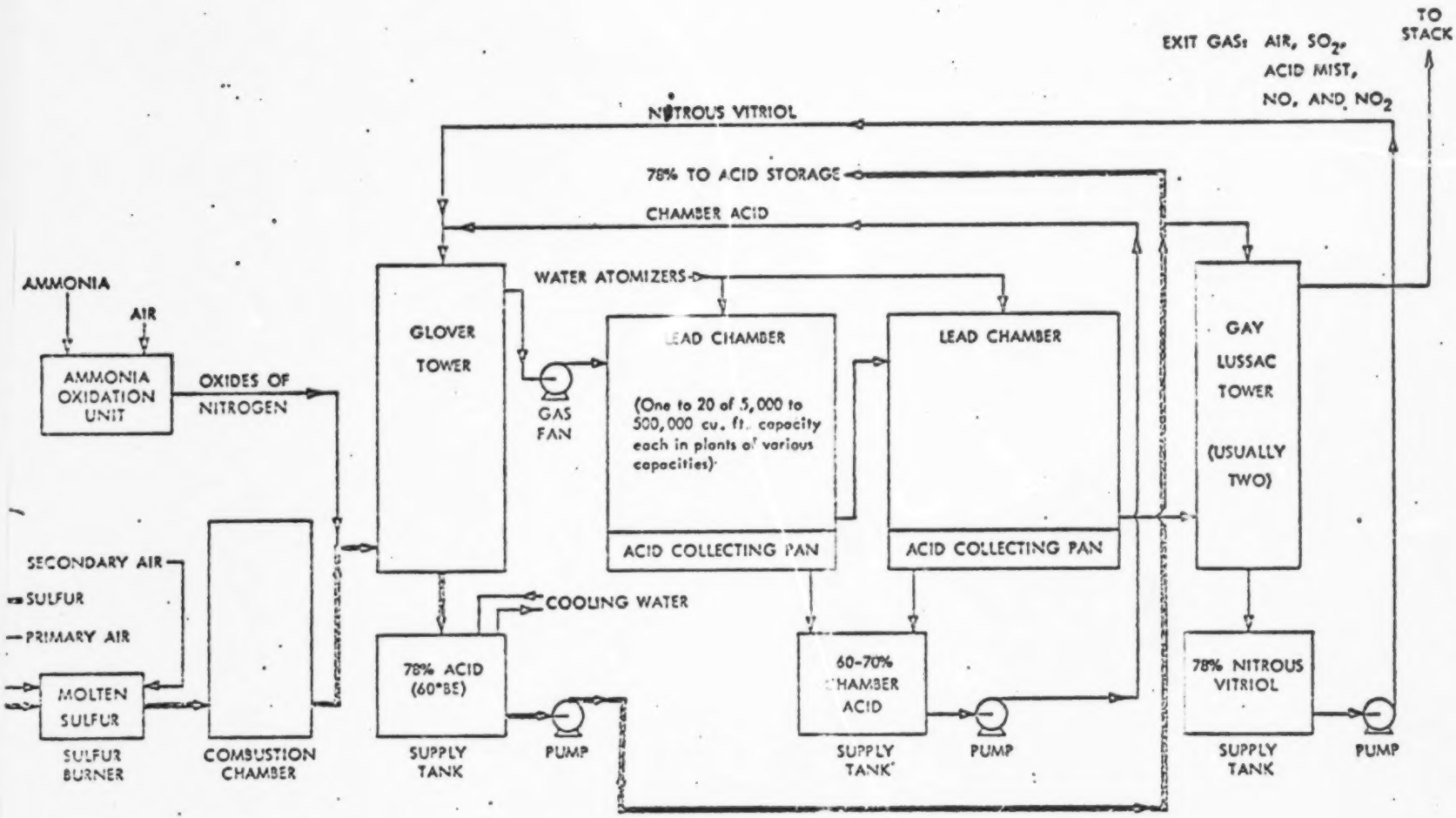


FIGURE 1. CHAMBER PROCESS SULFURIC ACID PLANT

(USES ELEMENTAL SULFUR AS RAW FEED)

In the Glover tower and ensuing chambers, the sulfur dioxide is oxidized in the presence of nitrogen oxides to form sulfur trioxide which combines with the water vapor to produce sulfuric acid.

The function of the Gay Lussac towers is to recover the released nitrogen oxides. The final tower is fed with 60° Bé sulfuric acid from the Glover tower, preferably at no more than 100°F and the nitrogen oxides are absorbed to form nitrosulfuric acid ($SO_5NH$).

The acid made in the lead chambers, ranging between 62 and 68%, is pumped to the top of the Glover tower, flows through counter-current to the hot sulfur dioxide gas and is thus concentrated to 78%. In addition, the Glover tower decomposes the nitrosulfuric acid and thus releases the nitrogen oxides for reuse.[3]

## 2.2 Contact Process

Figure 2 is a process schematic for contact sulfuric acid plant burning elemental sulfur. Sulfur is combusted in the sulfur burner to form a gas which is approximately 8% sulfur dioxide, 13% oxygen, and 79% nitrogen. The air used in the combuster is dried by passing it through a tower circulating

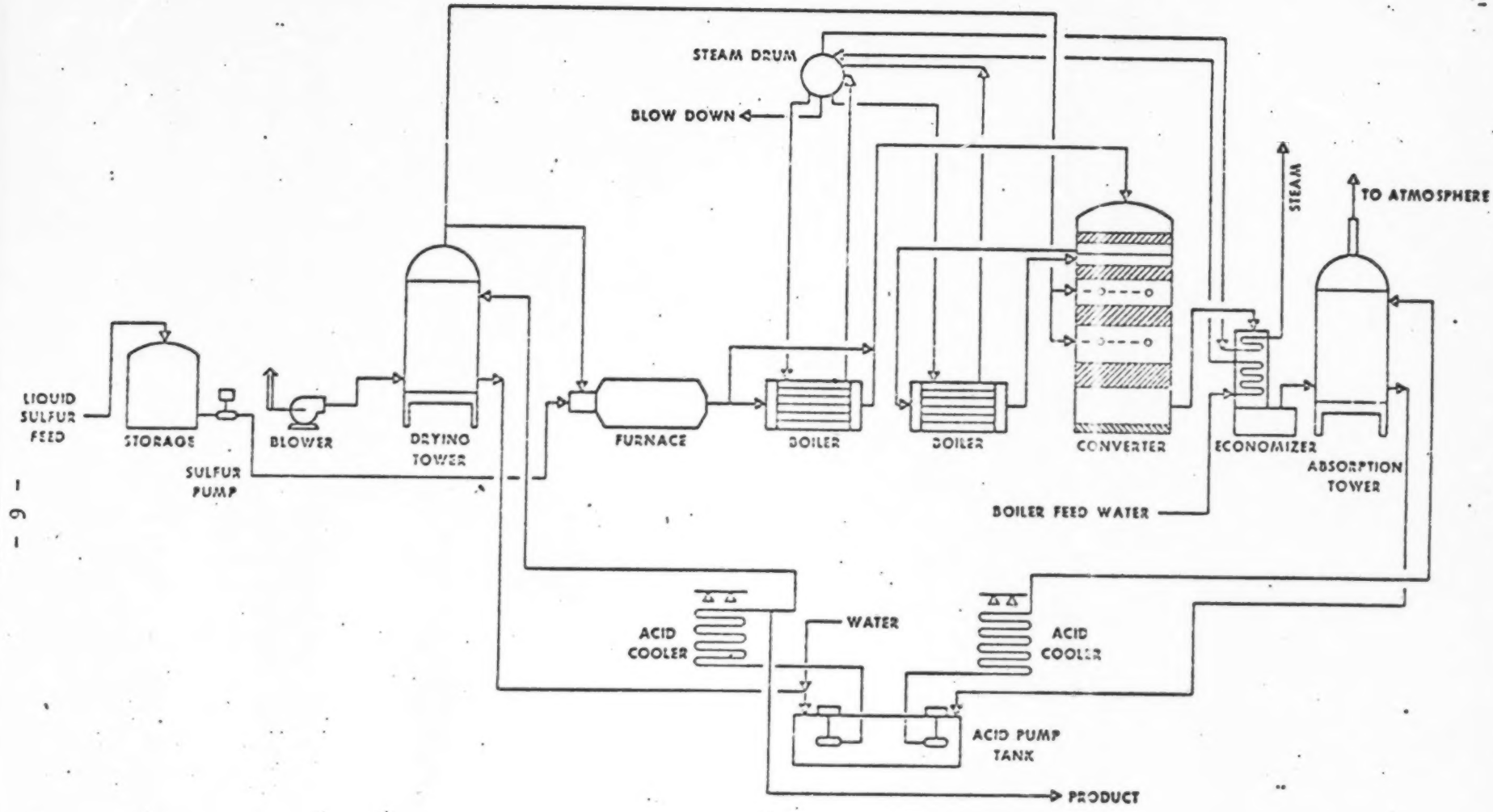


FIGURE 2. CONTACT PROCESS SULFURIC ACID PLANT

(USES ELEMENTAL SULFUR AS RAW FEED)

98% sulfuric acid. This is necessary to minimize acid mist formulation and the possibility of corrosion from occurring throughout the remainder of the plant.

The $SO_2$ is then oxidized in a converter in the presence of a catalyst containing vanadium pentoxide. Due to the exothermic reaction and the adiabatic conditions, the temperature of the reacting gas mixture increases as the composition of the gas approaches equilibrium conversion. In order to obtain additional conversion, the gas must be cooled; this requires several conversion stages with associated intermediate gas cooling.

The gas exiting from the converter is cooled in an economizer to between 450 and 500°F and the $SO_3$ is then absorbed in a circulating stream of 98% acid. The sulfur trioxide combines with the water in the acid to form additional acid, and water is in turn added to the acid to maintain the desired concentration.

If oleum is produced, the sulfur trioxide containing gases are first passed through an oleum tower which is fed with acid from the 98% absorption system. Effluent gas from the oleum tower is passed through the 98 percent absorber for recovery of residual sulfur trioxide.

## 2.3 "Wet Gas" Process

The metallurgical-type contact plant, shown in Figure 3, is more elaborate and expensive than a sulfur-burning plant. However, when the price of sulfide ore or smelter gas is low in comparison to sulfur, this type of plant may produce sulfuric acid at a lower cost than is possible in a sulfur burning plant. Metallurgical based plants account for about 15% of total sulfuric acid production in the United States.

Sulfur dioxide gas from smelters is available from such equipment as copper converters, reverberatory furnaces, roasters, and flash smelters. The sulfur dioxide concentrations and temperatures of these gases are often highly variable. When pyrites or zinc concentrates are the raw material, the effluent gas stream usually contains 7 to 14 percent sulfur dioxide.

The gas stream bearing the sulfur dioxide is contaminated with dust, acid mist, and gaseous impurities, which must be removed if a high-quality acid is to be produced. To remove the impurities, and the excessive amounts of water vapor, the gases are cooled to essentially ambient temperature and passed through purification equipment such as cyclone dust collectors and electrostatic precipitators.

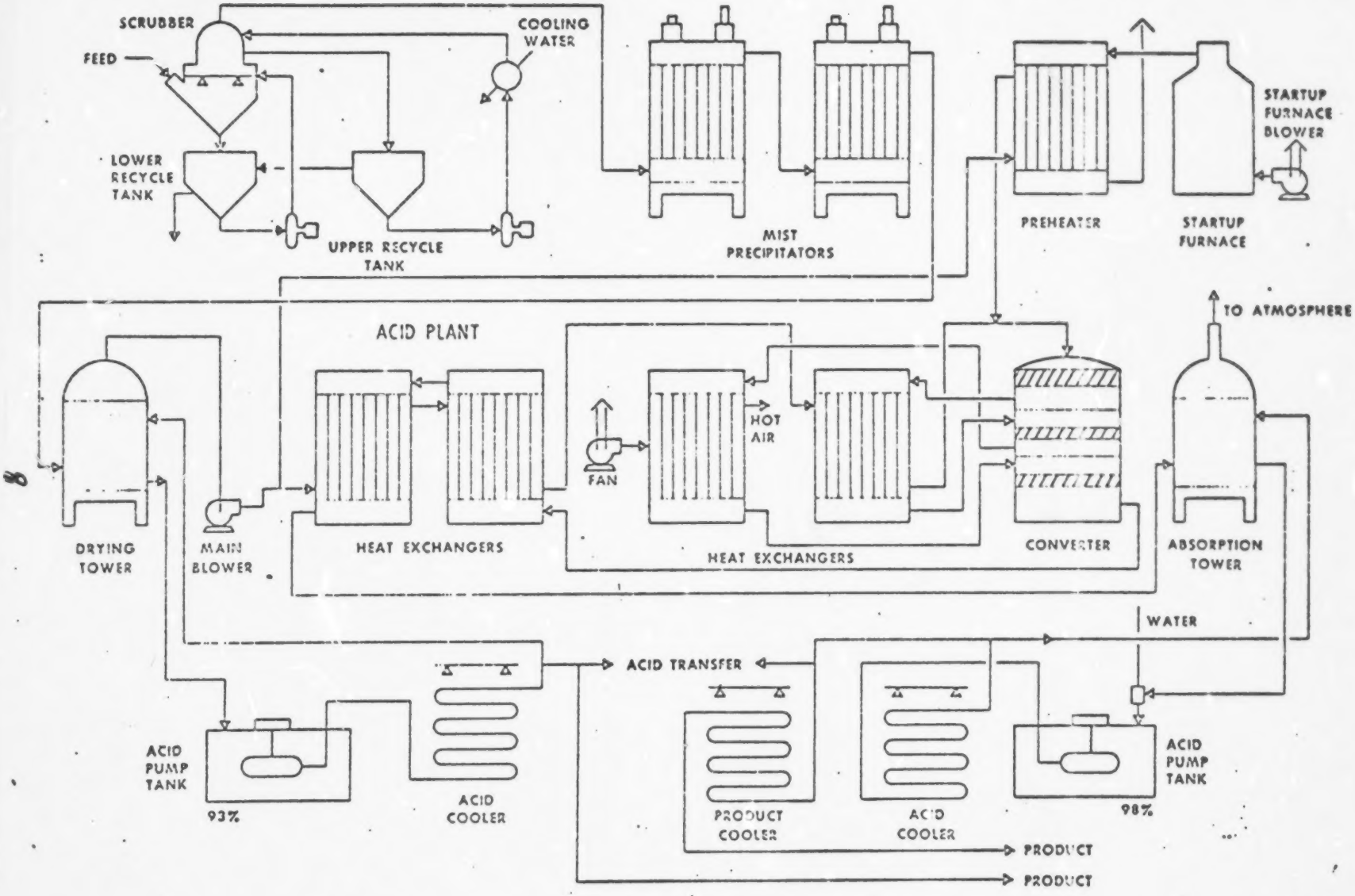


FIGURE 3. "WET GAS" SULFURIC ACID PLANT

After the gases are adequately cleaned and the excess water vapor removed, they are scrubbed with 66° Bé sulfuric acid which removes substantially all of the remaining water vapor. From this point on, this type of sulfuric acid plant is very similar to one burning elemental sulfur.

Plants that burn spent acid and hydrogen sulfide are similar to plants processing ores and smelter gas but are simpler and require less capital investment. However, investment costs are higher than for sulfur-burning units.

The spent acid and/or hydrogen sulfide is introduced into the combustion chamber and burned with undried atmospheric air. If only spent acid is burned, auxiliary fuel may be required. A common procedure for spent-acid plants is to burn hydrogen sulfide, spent alkylation acid, and sulfur simultaneously. The effluent combustion gas rarely contains more than 14 percent sulfur dioxide, but temperatures may be as high as 2400°F. Spent-acid plants also have higher concentrations of nitrogen oxides and carbon dioxide in the sulfur dioxide gas stream than are encountered in contact plants using high-purity sulfur.

## 3.0 EMISSIONS FROM SULFURIC ACID PLANTS

### 3.1 Sulfur Dioxide

Sulfur dioxide emissions vary as a function of the percent $SO_2$ in the feed stream and the overall plant conversion efficiency (i.e., percent of $SO_2$ oxidized to $SO_3$). For sulfur burning plants, the inlet sulfur dioxide concentration to the catalytic converters normally ranges between 7.5 and 8.5%. However, it can be as high as 10.5%. Conversion efficiency depends upon the number of stages in the catalytic converter and to a lesser extent, the amount of catalyst used. For the most part, plants built prior to 1960 had only three conversion stages and overall conversion efficiencies were approximately 95 to 96%. Sulfur burning plants built after 1960 generally had four stages and efficiencies normally ranged between 96 and 98%. Consequently, for three stage plants, $SO_2$ outlet concentrations range between 3000 and 5000 ppm and for four stage plants, between 1500 and 4000 ppm.

"Wet gas" sulfuric acid plants followed the same design trend. Three stage plants were mostly built prior to 1960 and four stage plants were usually built after 1960. Typical $SO_2$ concentrations in the converter feed and conversion efficiencies for various feed stocks are given in Table 3.1 on the following page.

TABLE 3.1 SULFUR DIOXIDE CONVERSION EFFICIENCIES FOR THREE AND FOUR STAGE CONVERTERS

| Feedstock | $SO_2$ in Converter Feed, Mol % | 3 Stage Converter Conversion Efficiency $SO_2$ to $SO_3$, % | 4 Stage Converter Conversion Efficiency $SO_2$ to $SO_3$, % |
|---|---|---|---|
| $H_2S$ | 7 | 94 to 96 | 95 to 98 |
| Pyrites | 6.5 to 7.5 | 94 to 96 | 95 to 98 |
| Acid Sludge | 6 to 8 | 94 to 96 | 95 to 98 |
| Copper Converter Gas | 3 to 7 | 90 to 95 | 94 to 98 |
| Roaster Gas | 5 to 7 | 94 to 96 | 95 to 98 |

The resultant emission ranges for sulfur dioxide are given in Table 3.2.

TABLE 3.2 SULFUR DIOXIDE EMISSIONS FROM THREE AND FOUR STAGE CATALYTIC CONVERTERS

| Feedstock | 3 Stage Converter $SO_2$ Content ppm by volume | 4 Stage Converter $SO_2$ Content ppm by volume |
|---|---|---|
| $H_2S$ | 3,000 to 5,000 | 1,500 to 4,000 |
| Pyrites | 2,500 to 5,000 | 1,500 to 4,000 |
| Acid Sludge | 2,500 to 4,000 | 1,500 to 5,000 |
| Copper Converter Gas | 2,000 to 10,000 | 2,000 to 7,000 |
| Roaster Gas | 2,000 to 5,000 | 1,000 to 4,000 |

Dual absorption plants have either four or five conversion stages and can operate with the same feed stocks as conventional single absorption plants. Of course, the economics may differ substantially from the conventional plant. Conversion efficiencies of 99.5% are readily obtainable and a few plants are operating with conversion efficiencies as high as 99.9%. Thus, it is possible to have sulfur dioxide emissions as low as 100 ppm with a rather conservatively designed plant and at approximately 500 ppm with only a moderate increase in cost and complexity over a conventional plant. The economics of various configurations of dual absorption, the effect of inlet $SO_2$ concentration on cost and efficiency, and examples of plants achieving a high degree of conversion efficiency are presented in the section on control technology.

## 3.2 Acid Mist

Acid mist is formed when the temperature falls below the $SO_3$ dew point and the water vapor present in the gas reacts with the $SO_3$. Once formed, this mist is extremely stable and much of it passes through the absorber. The quantity and particle size distribution of acid mist are a function of the type of sulfur feed stock and strength of the acid produced.

In elemental sulfur burning plants, dry sulfur is burned in dry air and hence there is little water vapor available for mist formation. However, when dark or contaminated sulfur is burned, the hydrocarbon impurities present in the sulfur burn to produce water vapor and this in turn combines with the $SO_3$ to form acid mist as the gas cools in the economizer or absorption tower.

In oleum producing plants, a greater quantity and a much finer mist is produced. Approximately 85 to 95 weight percent of the particles are less than 2 microns in diameter as compared to about 30 percent less than 2 microns in diameter for 98 percent acid production. Acid mist emission prior to any control equipment averages between about 5 to 10 mg/SCF for sulfur burning contact plants producing no oleum and about 15 to 30 mg/SCF for those plants producing oleum.

In "wet gas" plants, the formation of mist is inevitable since in the inlet $SO_2$ bearing stream, there are traces of $SO_3$ which combine with the available water vapor. The acid mist is normally removed and the gas dried in an absorbing tower prior to oxidation of the $SO_2$ to $SO_3$ in the catalytic converters.

Inlet loadings to the gas purification equipment in "wet gas" plants are usually between 50 and 60 mg/SCF. High efficiency, mist collection is practiced in almost all plants with the exception of a few of the $H_2S$ burning plants where the undried gas is reacted in the converter and mist formation is deliberately permitted. In this latter case, the entire output of the plant is initially in the form of acid mist rather than sulfur trioxide as it is in all other plants. If such a plant operated with a 7% sulfur dioxide gas entering the converter and at a 96% conversion efficiency, the gas leaving the converter, after cooling, would contain approximately 8500 mg of sulfuric acid per standard cubic foot. Much of this mist is recovered in the gas cooling equipment and the remainder recovered by use of high efficiency mist eliminators or electrostatic precipitators.[4]

Nitrogen oxides present in the converter gas also cause acid mist emissions since they reduce the efficiency of the absorption towers. The nitrogen oxides may result from the fixation of atmospheric nitrogen in high temperature sulfur furnaces, but more commonly are due to the nitrogen compounds contained in the sulfur feed stocks; spent acids from alkylation reactions are the most likely to produce them. Formation of nitorgen oxides can be avoided by choosing the correct

operating conditions for the reactor (decomposition furnace, roaster, etc.) in which they are formed. For instance, in the decomposition of spent acid containing nitrogen compcunds, operation of the furnace at about 2,000°F and a low oxygen content will ensure the decomposition products do not contain more than 100 ppm of nitrogen oxides.[5]

### 3.3 Visible Emissions

Acid mist emissions can create a very visible plume from a sulfuric acid plant stack. The visibility of the plume, however, is a much stronger function of particle size distribution than it is particle concentration since particles between 0.1 and 1 to 3 microns in diameter scatter light very effectively. Thus, if a large percentage of the particles being emitted from the absorber are less than about 3 microns, a heavy plume will result. This accounts for the dense plumes often present when oleum is being produced and no acid mist collection equipment is used. The MCA-PHS study[6] states that a plume would be visible if a large percentage of particles were less than 10 microns and concentrations exceeded 1 mg/SCF. Conversely, exit gas containing in excess of 5 mg/SCF may be invisible if the particles were substantially over 10 microns.

In a discussion of acid mist, it is necessary to distinguish between acid mist, gaseous $SO_3$, and sulfuric acid vapor.

At the acid plant temperatures, $SO_3$ is a colorless gas and therefore invisible. If present in the stack gas as a result of poor absorber operation, it will combine with water vapor in the atmosphere when it leaves the stack and produce a visible mist. The only way of preventing this mist formation is to ensure that through proper absorber design and operation, the $SO_3$ content of the gas leaving the tower is very low.

The stack gas leaving the absorption tower will always contain sulfuric acid vapor which will be in substantial equilibrium with the absorber acid. The only way this can be reduced is by cooling, and the vapor may in fact condense in the long ducts leading to the stack or in the stack itself. It is sometimes carried out of the stack as relatively large droplets which fall in the vicinity of the plant. Since operation of the absorption tower at low temperatures may make good absorption more difficult to achieve, it is necessary to strike a proper balance between a high $SO_2$ content on the one hand and a high acid vapor content on the other.

Thus, when establishing acid mist emission standards, it is necessary to stipulate whether total acid, which includes acid mist, $SO_3$ and $H_2SO_4$ vapor, or only acid mist emission per se is being regulated.

## 4.0 CONTROL TECHNOLOGY

### 4.1 Contact Process Plants - Sulfur Dioxide Control

There are many processes available for controlling $SO_2$ emissions from contact sulfuric acid plants. However, in this report we have concentrated on those which would find both the widest application and are either presently in use or could be used at this time. Other processes which have operated successfully but would now find only limited, if any, use in the United States, have not been extensively reviewed. Thus, a process like the ammonium sulfite-bisulfite absorption of $SO_2$ to produce ammonium sulfate, which has operated successfully in Europe and in the United States to reduce $SO_2$ emissions to 300 ppm,[7] would be a very unlikely candidate in the United States because of the poor market for the by-product. It's possible to exclude processes like these from consideration because other processes which are more economical can control emissions to at least the same extent.

Of the available processes, there are a minimum of five which would be closely evaluated by any sulfuric acid manufacturer who finds himself in the position of either building a new contact plant or reducing emissions from an existing one. The processes, which are listed on the next page, are:

1. Dual absorption
2. Sodium sulfite-bisulfite scrubbing (Wellman-Lord)
3. Magnesium oxide absorption of $SO_2$ with $SO_2$ recovery (Chemico)
4. Cat-ox (Monsanto)
5. SNPA - Topsoe (Haldor-Topsoe)

Of these five, the dual absorption and sodium sulfite-bisulfite scrubbing process will be discussed in detail, since they are presently in use in the United States. However, because of local plant conditions, one of the other five processes or perhaps one not mentioned, might be selected.

4.1.1 Dual Absorption

For new sulfuric acid plants, the dual absorption process is generally considered to be the most advantageous. The process introduces no new or unfamiliar techniques to the acid plant operation. Over 20 plants of this type have been operating satisfactorily in Europe for several years using both elemental sulfur and roaster gas as feed. For existing plants, it's also one of the more acceptable control alternatives if space is available and the inlet $SO_2$ concentration to the plant does not fall below about 3%.

In the dual absorption process, Figure 4, a greater proportion of the sulfur dioxide in the feed to the converter is converted to sulfuric acid. The $SO_3$ formed after partial conversion in two or three stages is removed in a primary absorption tower and the remainder of the gas, now with very high $O_2/SO_2$ ratio is returned to the converter. Because the $O_2/SO_2$ ratio in the partially absorbed gas is very high (at least 4:1 instead of 1.5:1), the equilibrium conversion is much greater and the second half of the converter, with either one or two stages of catalyst, will ensure that at least 99.5% of the original $SO_2$ content of the gas is fully oxidized. This high potential conversion is not affected greatly by the gas composition in the first part of the converter. Because of this, it is possible to operate these stages at a higher $SO_2$ inlet concentration than normal thereby permitting a reduction in equipment size. This reduction in size in part covers the cost of the additional equipment required for the intermediate absorber stage. Typically, a sulfur burning plant will operate at between 10 to 12% $SO_2$ inlet concentration as compared to 8% in the conventional single absorption plant.

The dual absorption process can be applied equally well to sulfur burning or wet gas plants. A wet gas plant will also operate at a higher $SO_2$ concentration than usual if this is

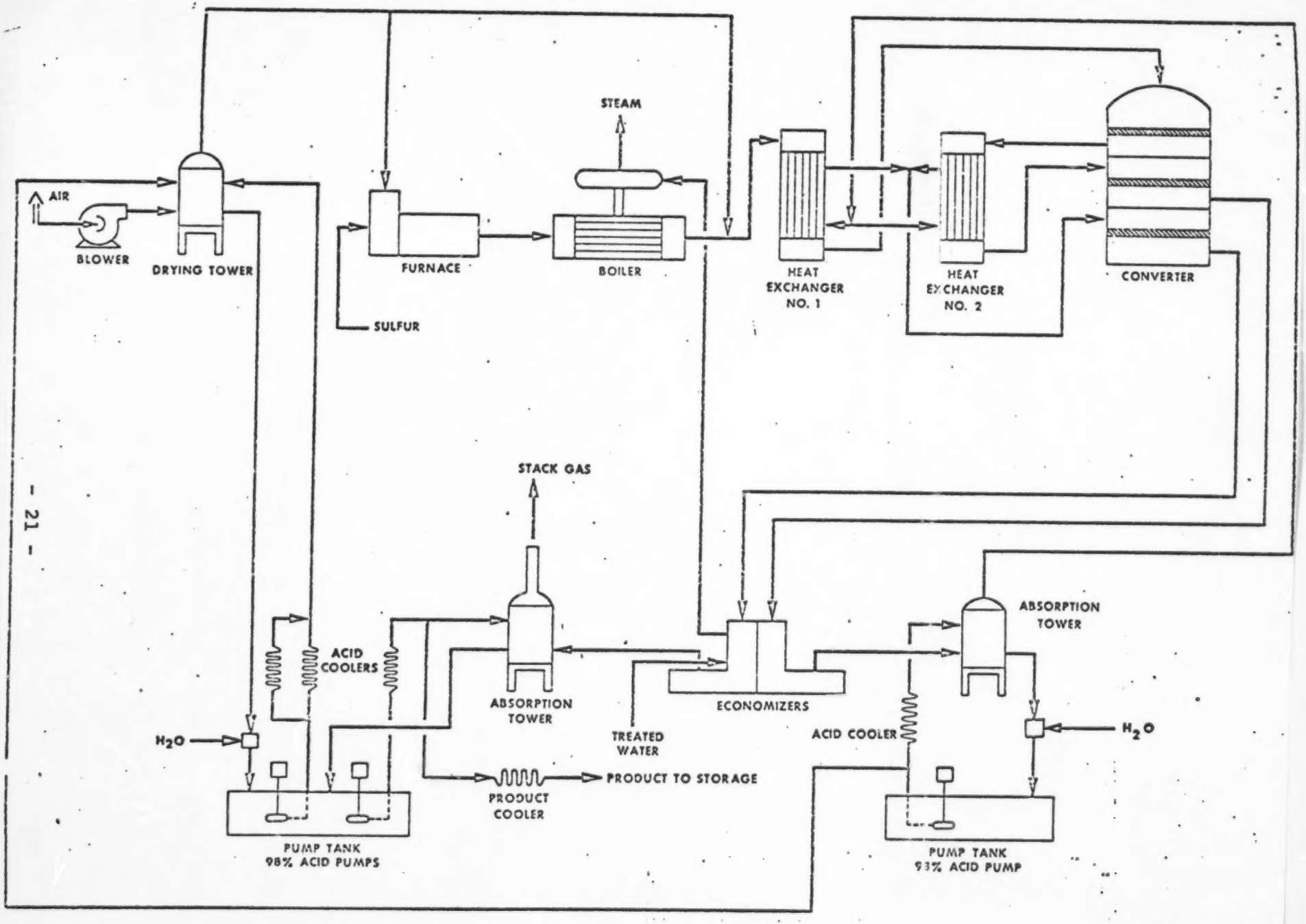


FIGURE 4. DUAL ABSORPTION SULFURIC ACID PLANT

available, as normally is the case when $H_2S$, pyrites or spent acid is the raw material.

The wet gas absorption plant contains two reheat cycles instead of one. It is thus more sensitive to low inlet $SO_2$ concentrations because enough heat may not be generated to maintain the thermal balance. Thus the process is more difficult to apply to plants operating on a smelter gas, where the inlet $SO_2$ content varies considerably, than it is on plants where the inlet $SO_2$ content is more constant, such as on pyrites, spent acid or sulfur based plants. For instance, if a plant is designed to operate on a copper converter gas varying cyclically between 3% and 8% $SO_2$, the converter stages which follow the first absorption stage will operate well at the 8% level. But when the concentration falls to 3%, practically all the conversion will take place in the primary stage and little heat will be generated in the secondary catalyst stage causing the temperature to fall below the reaction point. When the gas strength recovers, it will be some time before the catalyst in this last stage becomes active and thus there will be a period of poor conversion. Although this problem could be mitigated by different arrangement of heat exchangers, it would probably be necessary to use external heat in a converter preheater to maintain proper converter temperatures.

A dual absorption plant requires little more space than a conventional single absorption plant. Although it includes an additional absorber, the size of much of the equipment is smaller than in a conventional plant because of the high inlet $SO_2$ concentration.

The dual absorption process requires no different types of equipment than the conventional single absorber design. This means that the on-stream factor should be the same and the plant should require no additional operators.

Outlet $SO_2$ concentrations from a dual absorption plant can be reduced to less than 100 ppm. However, this requires careful design and relatively high costs.

If dual absorption is added to existing single absorption plants, the heat necessary to re-heat the gas after it exits from the primary absorber, can be provided by either heat exchange with the converter gas, mixing in a small quantity of gas directly from the sulfur furnace, or by using an outside heat source. The choice is dictated by individual plant considerations such as availability of waste steam. Of course, the economics change somewhat for each of these methods.

4.1.2 Tail Gas Recovery Systems

Tail gas recovery processes are generally applicable to all classes of contact acid plants. They usually provide simultaneous control of $SO_2$, $SO_3$, and acid mist with control of $SO_2$ to well below 500 ppm under normal operating conditions. The greatest technical drawback at present is that most are not completely developed.

The only tail gas recovery process presently operating in the United States on a sulfuric acid plant is the Wellman-Lord Process on the Olin plant in Paulsboro, New Jerney. At present, this unit is not working properly because of excessively high $SO_2$ inlet concentrations due to a malfunctioning in the acid plant.

In the Wellman-Lord Process, the tail gases are first scrubbed in a high pressure drop venturi with a sulfuric acid solution to remove acid mist and $SO_3$. Depending upon inlet concentrations, very high mist and $SO_3$ removal efficiencies can be obtained (in the order of 99%). Following this, the $SO_2$ is absorbed in two stages with sodium sulfite-bisulfite solutions. A sodium bisulfite is formed and a bleed stream is cooled to precipitate a sodium pyrosulfite. Water is then added to form a bisulfite-pyrosulfite slurry which is fed to a stream stripper where the pyrosulfite

dissolves to form bisulfite and the bisulfite decomposes to form sulfite and $SO_2$. The overhead gas is a saturated steam-$SO_2$ mixture which is cooled and the condensate is returned to the steam stripper and the highly concentrated $SO_2$ gas is cycled to the acid plant.

These costs decrease substantially as the size of the acid plant increases. For example, control costs for a 500 T/Day plant would be roughly $1.50/Ton and for a 1,000 Ton/Day plant about $1.00 per ton. Stauffer Chemical Company has estimated the control cost for a several thousand ton per day plant, consisting of several smaller plants, to be approximately $1.15 per ton of acid. It should be remembered that the cost bases used for these estimates could be different and that the cost estimated by Stauffer is for a specific plant which may or may not be representative of the industry. Yet the cost estimates are close and for large plants controlling to 500 ppm or below, the costs will be between $1.00 and $1.50 per ton.

Total sulfuric acid production costs vary between $11 and $13 per ton for sulfur burning plants in the size range of 250 T/D to 1,000 T/D. Thus the cost of control will add between 7 and 11% to production costs. However, the cost of sulfur contributes approximately $8/ton to the production cost, so the added cost of conversion is between 33 and 50% to reduce $SO_2$ emissions.

The SNPA-Topsoe process is presently operating on a sulfur recovery unit in Lacq, France. The process was jointly developed by Ste. Nat. de Petroles d Aquitaine (SNPA) and Haldor Topsoe, a Danish Engineering firm. The process catalytically oxidizes $SO_2$ to $SO_3$ and subsequently produces a 92 to 93% acid. The outlet concentration at Lacq is 1700 ppm of $SO_2$ but there are no inherent reasons why emissions can't be less than 500 ppm. However they will not at this time guarantee emissions below 400 ppm. For a 430 Ton/Day sulfur recovery plant emitting between 8000 and 9000 ppm, battery limit capital costs to reduce $SO_2$ to 500 ppm are approximately $1.5 million for both the SNPA-Topsoe and Wellman-Lord sodium sulfite system.

The Monsanto Cat-Ox process also catalytically oxidizes $SO_2$ to $SO_3$ but the major disadvantage is that it produces a weak acid, about 72-73%. Unless there is a ready market for the weak acid or the weak acid can be used in the plant without disrupting the thermal balance, this process would probably not be used.

The Lurgi Sulfacid process has similar limitations because it produces a weak acid. To the extent that a process produces a weak acid, it is undesirable because of the possible disruption of the plants thermal and water balances.

The Chemico-Basic process involves the absorption of $SO_2$ into a magnesium oxide-sulfite water slurry and then calcination to recover the $SO_2$ and magnesium oxide. The process can reduce $SO_2$ emissions, for example from 2000 ppm to 100 ppm. Although this process is not yet in commercial operation, a pilot scale unit has been operated successfully on an acid plant.

Because the necessary process equipment, such as calciners, may not be available with small enough capacity, this process is best suited for plants producing over 1000 tons/day.

Approximate capital investment costs for the different processes are presented in Table 4.1.[8]

## 4.2 Chamber Process Plants - Sulfur Dioxide and Acid Mist Control

Chamber process acid plants are relatively few in number, relatively small in capacity, and have an emission problem which is different from the contact process plants. Processes applicable to controlling emissions from contact plants are not suitable for removal of nitrogen oxides and, likewise, processes applicable to nitric acid plants for $NO_x$ control are not best suited for $SO_2$ control. Mist loadings are similar to those for non-oleum contact plants, and the same types of mist control devices are applicable.

TABLE 4.1

APPROXIMATE CAPITAL INVESTMENT REQUIREMENTS

FOR VARIOUS

$SO_2$ CONTROL SYSTEMS APPLIED TO 250 T/D $H_2SO_4$ PLANTS

| PROCESS | SULFUR BURNING 5000 PPM EMISSION | | | SULFUR BURNING 2500 PPM EMISSION | | | SULFUR BURNING 4000 PPM EMISSION | | | SMELTER GAS 3200 PPM EMISSION | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ADD'L ACID T/D | CONT. EFF. PPM | CAP. COST $ M | ADD'L ACID T/D | CONT. EFF. PPM | CAP. COST $ M | ADD'L ACID T/D | CONT. EFF. PPM | CAP. COST $ M | ADD'L ACID T/D | CONT. EFF. PPM | CAP. COST $ M |
| Dual Absorption (1) | 11.9 | 500 | 515 | 6.0 | 500 | 513 | 9.1 | 500 | 513 | N/A | N/A | N/A |
| Dual Absorption (2) | 40.5 | 500 | 485 | 34.6 | 500 | 482 | 38. | 500 | 482 | N/A | N/A | N/A |
| Dual Absorption (3) | 11.0 | 500 | 485 | 6.0 | 500 | 482 | 9.1 | 500 | 482 | N/A | N/A | N/A |
| Dual Absorption (4) | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | 7.0 | 500 | 620 |
| MgO Absorption | 12.5<br>12.5 | 250<br>250 | 550<br>570 | 6.2<br>6.2 | 125<br>125 | 470<br>490 | 10<br>10 | 200<br>200 | 510<br>530 | 7.0<br>7.0 | 160<br>160 | 575<br>600 |
| $Na_2SO_3$-$NaHSO_3$ Absorption | 12.5 | 250 | 610 | 6.2 | 125 | 540 | 10 | 200 | 585 | 7.0 | 160 | 640 |

(1) Add-On Dual Absorption Using Converter Heat.

(2) Add-On Dual Absorption Using Furnace Heat with Additional Sulfur Firing to Take Advantage of Higher Possible $SO_2$ Inlet Concentrations.

(3) Add-On Dual Absorption Using Furnace Heat Without Additional Sulfur Firing.

(4) Add-On Dual Absorption Using Outside Heat Source

The Chemico Report[9] summarizes the control potential for chamber plants very well when it reports, "A cursory review of the control cost for absorption of $SO_2$ and $NO_x$ using sodium hydroxide when applied to a rather large capacity chamber plant, gave a control cost of over $8 per short ton. This is far in excess of the control costs for contact plant control processes. Based upon this finding, it is considered very doubtful that a chamber acid plant, if faced with a choice of installing a control system or shutting down, could justify economically the installation of a control system.

## 4.3 Control of Sulfuric Acid Mist Emissions

From a plume visibility standpoint, plants producing a maximum of 99% acid (i.e. no oleum) often have clean stacks if bright, or uncontaminated, sulfur is used and the absorber is operating properly. However, plants producing oleum generally need either high efficiency electrostatic precipitators or high efficiency mist collectors. Table 4.2 presents the Chemico[10] report summary of"feasible systems" for acid mist control.

Although it is technically possible to get down to 0.1 mg/SCF for oleum plants using an electrostatic precipitator or a very high pressure drop tubular mist eliminator, it is not necessarily economically practical.

TABLE 4.2 FEASIBLE SYSTEMS FOR ACID MIST CONTROL

| | | Efficiency >3 Microns | Efficiency <3 Microns | Emission Level 99% Acid Plants[a] | Emission Level Oleum Plants[a] |
|---|---|---|---|---|---|
| 1. | Dual Mist Pads | 99+% | 15-30% | to 2 mg/SCF | to 5 mg/SCF |
| 2. | Tubular Type Mist Eliminator | 100 % | 95-99+% | 0.1 mg/SCF | 0.1 mg/SCF |
| 3. | Panel Type Mist Eliminator | 100 % | 90-98% | 0.5 mg/SCF | 0.5 mg/SCF |
| 4. | Electrostatic Precipitator | 99 % | Near 100% | 0.1 mg/SCF | 0.5 mg/SCF |
| 5. | Venturi Scrubber | 98 % | Low | 3 mg/SCF | Ineffective with 3 micron mist. |

a) Based upon manufacturers' generally expected results.

The Division of Air Pollution Control for the St. Louis Air Pollution Control District has reported that the National Lead Company has installed a high efficiency York Type S mist eliminator and has reduced sulfuric acid and $SO_3$ emissions to 0.65 mg/SCF. This plant, however, does not produce oleum.

No test data were obtained for acid mist collectors operating on oleum plants. However, there are several published reports of units stated to be operating with collection efficiencies in excess of 97% for particles smaller than 3 microns in diameter.[11]

Table 4.3 shows the efficiencies which can be expected from Brink's mist eliminators. High efficiency requires a high pressure drop and correspondingly increases operating cost. For an electrostatic precipitator, increased collecting area would be required and the capital investment would increase.

TABLE 4.3 OPERATING CHARACTERISTICS OF VARIOUS TYPES OF FIBER MIST ELIMINATORS AS USED ON SULFURIC ACID PLANTS

| Controlling Mechanism for Mist Collection | High Efficiency Brownian Movement | High Velocity Impaction | Spray Catcher Impaction |
|---|---|---|---|
| Superficial velocity (ft./min.) | 15 to 40 | 400 to 500 | 400 to 500 |
| Efficiency on particles greater than 3 microns | Essentially 100% | Essentially 100% | Essentially 100% |
| Efficiency on particles 3 microns and smaller | 95 to 99+% | 90 to 98% | 15 to 30% |
| Pressure drop ("W.C.) | 5 to 15 | 6 to 8 | 1/2 to 1 |

The Bay Area Air Pollution Control District has made several tests on electrostatic precipitators and reported a range of outlet loadings between approximately 0.02 and 0.04 grains/SCF (about 1.3 to 2.6 mg/SCF).

Monsanto-Enviro-Chem Systems, Inc. can typically offer guarantees of either 1 or 2 mg/SCF of $H_2SO_4$ depending upon

the type of acid plant and Brink mist eliminator used. However, when $H_2SO_4$ and $SO_3$ vapor in addition to acid mist is considered, they think a guarantee of 3 mg/SCF is feasible.

Again, the extent to which emissions are controlled is a matter of economics. The approximate investment costs for different types of acid mist control systems is shown in Table 4.4.[12]

The costs for acid mist control are a small fraction of the total plant investment cost. Thus, control of emissions to between 1.0 and 2.0 mg/SCF of total acid is certainly possible for almost all types of sulfuric acid plants. Of course some types of plants, such as elemental sulfur burning plants producing a maximum strength acid of 99%, could control emissions to somewhat less than 1.0 mg/SCF.

TABLE 4.4 APPROXIMATE CAPITAL INVESTMENT REQUIREMENTS FOR VARIOUS ACID MIST CONTROL SYSTEMS

| | New Plants | | | |
|---|---|---|---|---|
| Control System | 50 T/D (3,750 ACFM) | 250 T/D (18,700 ACFM) | 750 T/D (56,000 ACFM) | 1,500 T/D (112,000 ACFM) |
| Dual Mesh Pads | $10,000 | $20,000 | $ 28,000 | $ 38,000 |
| Tubular Fibre Type | 55,000 | 70,000 | 105,000 | 170,000 |
| Panel Fibre Type | 14,000 | 23,000 | 55,000 | 95,000 |
| Electrostatic | 60,000 | 85,000 | 105,000 | 200,000 |
| Venturi Scrubber | | 70,000 | | |

| | Existing Plants | | | |
|---|---|---|---|---|
| Control System | 50 T/D (3,750 ACFM) | 250 T/D (18,700 ACFM) | 750 T/D (56,000 ACFM) | 1,500 T/D (112,000 ACFM) |
| Dual Mesh Pads | $13,000 | $ 25,000 | $ 35,000 | $ 48,000 |
| Tubular Fibre Type | 78,000 | 100,000 | 150,000 | 240,000 |
| Panel Fibre Type | 27,000 | 44,000 | 105,000 | 170,000 |
| Electrostatic | 60,000 | 85,000 | 105,000 | 200,000 |
| Venturi Scrubber | | 70,000 | | |

NOTE:

Size and cost depends upon tail gas flow rate and on design efficiency.

Costs are given for sulfur burning plants.

Adjustments proportional to gas flow must be made for various wet gas plants.

## 5.0 SULFURIC ACID PLANTS UTILIZING BEST EMISSION CONTROL TECHNOLOGY

There are two plants in the United States where $SO_2$ control processes are in operation and are being closely evaluated by the industry. The first is the American Cyanamid plant in Linden, New Jersey, which has the only dual absorption plant presently operating in the United States. The second is the Olin Corporation plant at Paulsboro, New Jersey, where the Wellman-Lord scrubbing process is currently being brought on-stream.

The American Cyanamid plant was designed and constructed by Leonard Monsanto, has a capacity of 700 Tons/Day, uses elemental sulfur for the feed, and produces 93%, 98%, and oleum concentrations of acid. Conversion efficiency is guaranteed to be at least 99.5% and $SO_2$ emissions to be less than 500 ppm. As of early September 1970, the plant was not continuously operating at full capacity, but on the demonstration run at full capacity, the $SO_2$ emissions were less than 500 ppm.

Capital cost was approximately 5.5 million dollars, and it was estimated that the cost of the dual absorption over conventional single stage absorption amounted to one million dollars. This figure of one million dollars is in substantial agreement with the comparative costs range presented in the

paper by Monsanto on "Interpass Absorption".[13] Using 5.5 million dollars as the cost for the double absorption plant, the cost for a conventional plant would range between 4.7 and 4.9 million dollars, using the Monsanto figures, or an added cost of between 0.6 and 0.8 million dollars. See Appendix 1 for further cost breakdown.

The Olin plant at Paulsboro, New Jersey, is a 700 Ton/Day regenerative plant handling a variety of spent acids from the South Jersey-Greater Philadelphia area. Average $SO_2$ inlet to the recovery process is between 5000 and 6000 ppm.

As of late September 1970, the unit was not operating satisfactorily due to problems caused by both the acid plant and the Wellman-Lord process. However, a plant shutdown is scheduled for early October 1970, at which time the problems should be rectified. Wellman-Lord guarantees 90% removal and recovery of the $SO_3$ and $SO_2$ respectively and $SO_2$ stack emissions of less than 500 ppm.

The sulfuric acid plant with the lowest observed $SO_2$ emissions is the Sudchemie Kehlheim plant in Germany. This relatively small plant (6600 CFM) burns elemental sulfur, has an average conversion efficiency of 99.91% and an average $SO_2$ outlet concentration of 82 ppm. The inlet $SO_2$ concentration varies between about 9.0 and 9.3% and the conversion efficiency varies between 99.90 and 99.92.

Table 5.1 summarizes pertinent operating data for some European dual absorption plants. Additional information on the Sudchemie, Kehlheim plant is in Appendix 2.

The Toho Zinc Company at Akita, Japan, uses a dual absorption plant followed by tail gas scrubbing and probably has very low $SO_2$ emissions. However, emission numbers for this plant are not presently available.

The Division of Air Pollution Control for St. Louis County, reports that the National Lead Plant in St. Louis, Missouri, uses a York ~~Tape~~ Type S mist eliminator and has an average mist emission of 0.65 mg/SCF. This plant is a 400 Ton/Day plant burning elemental sulfur and producing no oleum. This average is based on four tests using the Shell Development method which measures $SO_3$, $H_2SO_4$ vapor, and acid mist. The range was 0.6 to 0.7 mg/SCF.

TABLE 5.1 OPERATING DATA FOR EUROPEAN DUAL ABSORPTION PLANTS

| Plant | $SO_2$ Source | Gas Flow (SCFM) | $SO_2$ Inlet Concentration Range % | Conversion Efficiency Range % | Outlet $SO_2$ Concentration Range % |
|---|---|---|---|---|---|
| 1. Farbenfabriken BAYER Leverkusen Werke Plant #1 | Roasting Sulfide Ore | 28,600 | 8.2 - 9.3 | 99.71 to 99.83 | 139 to 260 |
| Plant #2 | Elemental Sulfur | 27,100 | 8.5 - 9.2 | 99.78 to 99.83 | 148 to 202 |
| 2. Farbenfabriken BAYER Dormagen Werke | Roasting of Sulfide Ores | (490 Ton/ Day Plant | 9.0 - 9.7 (Avg. 9.4) | 99.27 to 99.5 | 510 to 790 |
| 3. Berzelius Metallhutten Homburg Zinkhutte | Roasting of Zinc Ore | 15,000 | 5.9 - 6.4 | 99.60 to 99.73 | 190 to 300 |
| 4. Sudchemie, Kehlheim | Elemental Sulfur | 6,500 | 9.09 - 9.73 | 99.90 to 99.92 | 74 to 91 |
| 5. Saurefabrik Schweizerhalle Basel, Switzerland | Elemental Sulfur | - | 9.9 to 10.5 | 99.48 to 99.81 | 220 to 600 |

## 6.0 SPECIFIC REGULATIONS PERTAINING TO EMISSIONS FROM SULFURIC ACID PLANTS

Several control districts are either considering or have established a sulfur dioxide emission limit of 500 ppm. The New Jersey State Department of Environmental Protection, Bureau of Air Pollution Control, has stipulated that sulfuric acid plants built after June 15, 1967, must not have sulfur dioxide emissions in excess of 500 ppm. Existing plants must control $SO_2$ emissions to 2000 ppm.

The St. Louis area has also established a maximum emission level of 500 ppm of $SO_2$ from new sources as stipulated in the following abstract from the Air Quality Standards and Air Pollution Regulations for the St. Louis Metropolitan Area, March 24, 1967:

> B. Concentration of Sulfur Compounds in Emissions Restricted
>
> 1. No person shall cause or permit the emission into the atmosphere from any existing source specified in subsection A (1) of this regulation, gases containing more than ~~2000~~ 500 parts per million by volume of sulfur dioxide from any new source.
>
> 2. No person shall cause or permit the emission into the atmosphere from any source specified in subsection A (1) of this regulation, gases containing more than 70 milligrams per cubic meter of sulfuric acid or sulfur trioxide or any combination thereof or 35 milligrams per cubic meter of sulfuric acid, sulfur trioxide or any combination thereof from any new source (expressed as sulfuric acid).

The City of Chicago has the most stringent $SO_2$ and acid mist emission standards. $SO_2$ emissions are limited to 500 ppm from both new and existing sources as stipulated in the following abstract from Chapter 17 of the Municipal Code of Chicago, Environmental Control Ordinance.

(4) Sulfur Oxides.

> No person shall cause or permit the emission into the atmosphere from any new or existing source gases containing more than 500 parts per million by volume of sulfur dioxide nor more than 15 milligrams per cubic meter of sulfuric acid or sulfur trioxide, or any combination thereof; provided, however, that the foregoing limitations shall not apply to those emissions in which both fuel is burned primarily to produce heat, and the sulfur compound emission is due primarily to the sulfur in the fuel burned.

## 7.0 RECOMMENDED EMISSION STANDARDS FOR NEW PLANTS

It is
~~It's~~ entirely possible, as demonstrated by the European plants, to restrict $SO_2$ emissions to approximately 100 ppm. However, it is not ~~clear~~ known how long these plants have been operating nor how these low emission levels can be maintained ~~and if it is possible to maintain these low emission levels~~ over a period of several years. Furthermore, because of different economic factors such as the market and price for sulfur and sulfuric acid, the cost for achieving these low $SO_2$ emission levels may not be justifiable in the United States.

From a consideration of the different processes available for $SO_2$ control and the associated cost for this control, an $SO_2$ emissions standard for sulfuric acid plants between 300 and 400 ppm certainly appears to be feasible.

Acid mist emissions are easier to control when no oleum is being produced and when elemental sulfur is the feed stock. However, it is feasible for all sulfuric acid plants to control acid mist emissions including $SO_3$ and $H_2SO_4$ vapor to between 1.0 and 2.0 mg, expressed as 100% $H_2SO_4$, per standard cubic foot.

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## APPENDIX 1

## COMPARATIVE COSTS FOR NEW DUAL ABSORPTION VS. SINGLE ABSORPTION PLANTS [12]

Cost of conventional plants taken as 1.0

| | Metallurgical (Cold Gas) | Sulfur Burning |
|---|---|---|
| Capital | 1.05 to 1.10 | 1.12 to 1.18 |
| Operating Costs | | |
| Raw Material | 0.98 | 0.98 |
| Labor | 1.00 | 1.00 |
| Electric Power | 1.15 to 1.25 | 1.20 to 1.30 |
| Cooling Water | 1.00 to 1.10 | 1.10 to 1.20 |
| Maintenance | 1.04 to 1.08 | 1.10 to 1.16 |
| Indirect Charges | | |
| Depreciation | 1.05 to 1.10 | 1.12 to 1.18 |
| General Overhead | 1.01 to 1.02 | 1.02 to 1.04 |

## APPENDIX 2. OPERATING DETAILS FOR THE SUDCHEMIE, KEHLHEIM PLANT

| Section | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Gas flow | $Nm^3/h$ | 11,700 | 11,700 | 11,700 | 11,700 | 11,800 | 11,800 | 11,700 | 11.730 |
| Converter, IN | $SO_2$ % | 9.23 | 9.09 | 9.23 | 9.09 | 9.09 | 9.23 | 9.09 | 9.15 |
| Converter, OUT | $SO_2$ % | 0.008 | 0.0091 | 0.0091 | 0.008 | 0.008 | 0.0074 | 0.0079 | 0.0082 |
| Total % conversion | % | 99.91 | 99.90 | 99.90 | 99.91 | 99.91 | 99.92 | 99.91 | 99.91 |
| Pressure at entrance to convertor | mm $H_2O$ | 1,276 | 1,278 | 1,285 | 1,298 | 1,305 | 1,260 | 1,270 | 1,282 |
| Catalyst I, IN | °C | 424 | 426 | 425 | 425 | 425 | 422 | 422 | 424 |
| " I, OUT | " | 579 | 579 | 578 | 578 | 578 | 574 | 577 | 577 |
| Catalyst II, IN | " | 459 | 459 | 459 | 459 | 458 | 458 | 458 | 459 |
| Catalyst III, IN | " | 452 | 458 | 457 | 457 | 456 | 456 | 457 | 457 |
| Intermediary heat exchanger, INPUT | " | 380 | 381 | 382 | 381 | 380 | 380 | 380 | 380 |
| " , OUTPUT | " | 230 | 231 | 232 | 235 | 233 | 232 | 232 | 232 |
| Absorber I, IN | " | 180 | 181 | 183 | 189 | 181 | 180 | 180 | 182 |
| Catalyst IV, IN | " | 406 | 409 | 412 | 407 | 405 | 406 | 405 | 407 |
| " IV, OUT | " | 419 | 420 | 420 | 420 | 418 | 418 | 419 | 419 |
| Absorber II, IN | " | 190 | 190 | 192 | 190 | 190 | 190 | 189 | 190 |
| Acid temperature in Absorber I | °C | 71 | 71 | 72 | 72 | 75 | 72 | 72 | 72 |
| Absorber II | " | 72 | 72 | 72 | 73 | 75 | 72 | 73 | 73 |
| Acid concentration in Absorber I | % | 99.11 | 99.12 | 98.85 | 98.98 | 98.5 | 98.5 | 98.82 | 98.85 |
| Absorber II | % | 99.05 | 99.05 | 98.95 | 99.37 | 98.75 | 98.67 | 98.76 | 98.92 |
| % Conversion in Catalyst layer I | % | 62.9 | 60.3 | 62.0 | 60.3 | - | 60.9 | 60.3 | 61.2 |